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Title: "Fixed-site-carrier composite membrane and process for producing the same"

The present invention relates to novel fixed-site-carrier composite membranes and a process for producing the same, as well as the use of such membranes for separation of carbon dioxide (CO<sub>2</sub>) from gas streams.

5 During the last couple of decades, concern for our global environment has brought into focus the need for CO<sub>2</sub> from anthropogenic sources being captured and brought into storage. Industry will in future have to comply with strict regulations on CO<sub>2</sub>-emissions, hence separation and recovery of CO<sub>2</sub> from gas streams has become of vital importance for industry from the viewpoint of environment and energy.

10

CO<sub>2</sub> capture is further desirable from various types of gas streams like fuel gas, biogas, natural gas, synthesis gas and breathing etc. that constitute a part of all kind of combustions, petrochemical industry, biogas production and life support systems.

15 In general, CO<sub>2</sub> is separated from gas mixtures with H<sub>2</sub>, CO, N<sub>2</sub> and CH<sub>4</sub> by reversible absorption methods employing various chemical and/or physical solvents. As the conventional process of treating CO<sub>2</sub> is highly energy consuming, the cost as well as the increased demand of environmental protection bring about a need for new processes with energy efficient and more selective gas treating technology.

20

The use of a membrane for separation is suggested as a method consuming lower energy [1,2].

A lot of research has been performed in order to obtain membranes having both high  
25 permeability and selectivity, as well as being stable and durable.

An approach to overcome the above limitations has been developed by casting carriers directly into polymeric membranes. These so-called fixed-site-carrier (FSC) membranes have carriers covalently bonded to the polymer backbone and the carriers have a  
30 restricted mobility.

CN-A-1363414 discloses the use of FSC membranes in the purpose of separating CO<sub>2</sub> and CH<sub>4</sub>. A process for preparing a composite membrane to separate carbon dioxide gas from hollow or flat membrane of polysulfone, polyacrylonitrile, or polyether sulfone  
35 through dipping in polyvinylamine solution for 5-60 minutes, crosslinking with 5-50 % glutaraldehyde solution for 5-40 minutes and the solution of sulphuric acid or hydrochloric acid for 5-30 minutes, drying and washing with water, is disclosed therein.

It has now surprisingly been found that by using FSC membranes similar to those reported in CN-A-1363414 and varying the crosslinking agents, controlling the molecular weight and swelling the membranes in water, a remarkably increase in selectivity for  $\text{CO}_2/\text{CH}_4$  is obtained, while the high permeability is maintained.

It is a main object of the present invention to provide membranes for the facilitated transport of  $\text{CO}_2$ .

Another object of the invention is to provide membranes achieving both high permeabilities and high selectivities for  $\text{CO}_2$  over gases like  $\text{CH}_4$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{CO}$ .

Still another object of the invention is to provide such membranes which are stable and durable.

These and other objects are achieved by a membrane comprising a support coated with crosslinked polyvinylamine, wherein the crosslinking agent is a fluoride containing compound, and wherein the said membrane is swelled in water vapour.

Furthermore, the present invention provides a process for producing a membrane as defined above, by preparing polyvinylamine with high molecular weight comprising high degree of amination; coating said polyvinylamine on a support to obtain a composite membrane; crosslinking the cast membrane with a fluoride containing compound; and swelling the crosslinked cast membrane in water vapour.

The present invention also comprises the use of a membrane as defined above, for separation of  $\text{CO}_2$  from gas mixtures.

In the following the invention will be further explained by examples and figures. The examples are just meant to be illustrative and shall not be considered as limiting.

#### Brief description of the Figures

Fig. 1 shows an experimental setup for gas permeation measurement.

Fig. 2 shows effect of molecular weight of PVAm on ideal selectivity of  $\text{CO}_2/\text{CH}_4$ .

Fig. 3 shows a proposed mechanism of facilitated transport in the fixed-site-carrier membrane.

Fig. 4 shows the influence of water on the permeation.



## EXAMPLES

Fixed-site-carrier (FSC) membranes were prepared by coating polyvinylamine (PVAm) on various supports such as polyethersulfone (PES), polyacrylonitrile (PAN), cellulose acetate (CA) and polysulfone (PSO). The cast PVAm on support was crosslinked by various methods using glutaraldehyde, hydrochloric acid, sulphuric acid and ammonium fluoride. The effect of molecular weight of PVAm and feed pressure on the permeance and selectivity was also investigated. The permeance and selectivity of the membranes were measured in water vapour swollen conditions.

### Acrylamide polymerization

The polymerization of acrylamide ( $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}_2$ ; Merck) was carried out according to well known procedures [3] using ammonium persulfate  $((\text{NH}_4)_2\text{S}_2\text{O}_8)$  and sodium sulphite ( $\text{Na}_2\text{SO}_3$ ) as initiators. Persulfate was decomposed by sulphite ion as the reducing agent, and the polymerization included the three basic steps; initiation, chain propagation and chain termination. The polymerization was allowed to proceed at  $45^\circ\text{C}$  for 5 h and  $55^\circ\text{C}$  for 2 h. The molecular weight of the resulting polyacrylamide (PAA) was determined by measuring the viscosity of the diluted polymer solution. The intrinsic viscosity of PAA in water was determined by using an Ubbelohde viscometer. PAA with different molecular weight could be obtained by controlling the concentration of initiators. The obtained PAA solution was pale yellowish, but clear and very viscous which depended on molecular weight and concentration of PAA.

### Preparation of polyvinylamine by Hofmann reaction of polyacrylamide

The Hofmann reaction was suggested as a quick and convenient method of preparing PVAm from PAA by Tanaka et al. [5-7]. After examination and extent investigation of Hofmann reaction, Archari et al. [4] proposed that PVAm could be prepared from PAA by the Hofmann reaction with high degree of amination (more than 90 %) keeping the extent of side reactions to a very low level by very careful control of reaction parameters. The amino group content in PVAm was measured to be over 90 mole %. The obtained product was a hygroscopic white solid. The final polymer was dissolved in water to a suitable concentration (5-10%) for membrane casting. The average molecular weight of PVAm was determined by the following relation:  $[\eta]/(\text{dL}\cdot\text{g}^{-1}) = 6.2 \cdot 10^{-3} M_\eta^{0.88}$  where  $[\eta]$  is the intrinsic viscosity in 0.01 M aqueous NaOH/0.1 M aqueous NaCl water at  $25^\circ\text{C}$  [4,7].

Main reaction:  $\text{R-CO-NH}_2 + \text{NaOCl} + 2 \text{NaOH} \rightarrow \text{RNH}_2 + \text{Na}_2\text{CO}_3 + \text{NaCl} + \text{H}_2\text{O}$

#### Membrane preparation

Two microporous polysulfone flat sheet support membranes (PSO) were tested: one  
 5 with a molecular weight cut-off (MWCO) of 20,000 (from Danish Separation Systems AS (DSS)) and one with MWCO of 30,000 (from Osmonics Vista Operation). The following supports were also tested: polyethersulfone (PES, MWCO 10,000) cellulose acetate (CA, MWCO 20,000) and polyacrylonitrile (PAN, MWCO 75,000) (all three from Osmonics Vista Operation).

10 The support membrane was cut into suitable pieces and taped to a clean, levelled glass plate. The casting polymer solution of PVAm was poured on the support, and film thickness adjusted by using a casting knife. The gap between the casting knife and the support membrane was set to approximately 20 $\mu\text{m}$ . The casting polymer solution was  
 15 evaporated at room temperature for at least 6 h.

A layer of PVAm (MW ~34 000) was clearly formed on DSS PSO. The thickness of the layer was about 5-10  $\mu\text{m}$ ; hence some of the solution has sifted down into the support. Meanwhile the PVAm (MW 39 000) layer was hardly visible for membranes coated on  
 20 Osmonics PSO.

The dried cast membranes were crosslinked by different procedures:

- (1) Glutaraldehyde (50%, 30 min);
- 25 (2) Glutaraldehyde (50%, 30 min), and then  $\text{H}_2\text{SO}_4$  (pH=1, 10-30 min);
- (3)  $\text{NH}_4\text{F}$  (0.5M, 2 h);
- (4) Glutaraldehyde (50%, 30 min), and then  $\text{NH}_4\text{F}$  (0.5 M, 2 h);
- (5)  $\text{H}_2\text{SO}_4$  (pH=1, 10-30 min) or  $\text{HCl}$  (pH=1, 10-30).

30 Procedure (2) above, is according to the crosslinking disclosed in CN-A-1363414.

Care was taken to ensure the membrane was levelled during drying and crosslinking processes in order to obtain an even and defect-free membrane. The crosslinked membranes were stored in a chamber saturated with water vapour.

35

#### Membrane testing

Permeability of the membranes was measured with an apparatus equipped with a humidifier (Fig. 1). A membrane was placed on a porous metal disk in a flat type membrane cell and was sealed with rubber O-rings. The feed gas was saturated with water vapour by a humidifier. The feed and permeate flow rates were measured by standard methods. All experiments were conducted in a constant temperature environment and the experiment temperature range was between 25-35°C and the pressure difference between the feed and the permeate sides was 2-4 bar.

The permeance (flux) was calculated as  $P/l$  in the units  $\text{m}^3 \text{ (STP)}/(\text{m}^2 \text{ bar h})$ . The flux is strongly dependent on the thickness of the membrane. For the membranes reported herein, the thickness was  $\sim 20\mu\text{m}$ . When the thickness is brought down to at least 1/10 of this, permeation is expected to increase correspondingly  $\times 10$ .

Permselectivity results of PVAm membranes cast on different support materials are compared in Table 1. As can be seen, PSO supported membranes showed much higher selectivity of  $\text{CO}_2$  over  $\text{CH}_4$ . CA, PAN and PES showed high permeance, but their selectivity was very small. Osmonics PSO which had no apparent PVAm layer showed lower permeance as well as lower selectivity than DSS PSO. The DSS PSO support seemed to be the most suitable support for the composite membrane and was therefore chosen in the further investigations.

**Table 1**

Comparison of membranes on different support materials in permselectivity<sup>a,b</sup>

Support	Polysulfone (DSS)	Polysulfone (Osmonics)	Cellulose acetate	Polyacrylonitrile	Polyethersulfone
$\text{CO}_2$ permeance <sup>c</sup>	0.00837	0.0063	0.099	0.0327	0.00388
$\alpha (\text{CO}_2/\text{CH}_4)$	1143	26.9	17.3	5.1	6.5

<sup>a</sup>Membrane preparation: Cast PVAm solution on supports, dried at room temperature, crosslinked with  $\text{NH}_4\text{F}$ , stored in chamber saturated with water vapour.

<sup>b</sup>All the data measured at 2 bar and room temperature.

<sup>c</sup>Permeance,  $P/l$ , in units of  $\text{m}^3 \text{ (STP)}/\text{m}^2 \text{ bar h}$ .

For the same crosslinking condition, the increase in molecular weight of polyvinylamine resulted in a significant decrease in permeation for  $\text{CH}_4$  and a remarkable increase in the selectivity. This corresponds clearly to molecular weight, and when this was more than 70,000, the increase of selectivity was remarkable. This is

shown in Fig. 2 where the effect of molecular weight of PVAm on ideal selectivity of  $\text{CO}_2/\text{CH}_4$  at  $35^\circ\text{C}$ , 3 bar, is plotted. The membrane preparation used in this experiment is cast PVAm solution on DSS PSO, dried at room temperature, and crosslinked with  $\text{NH}_4\text{F}$ .

The PVAm/PSO membranes were tested for two months and were still maintaining the high selectivity of  $\text{CO}_2/\text{CH}_4$ .

The results of different crosslinking methods are shown in Table 2. Among the five crosslinking methods, the crosslinking with  $\text{NH}_4\text{F}$  resulted in a surprisingly high selectivity.

**Table 2**

Comparison of methods of crosslinking in permselectivity for PVAm membranes cast on PSO support<sup>a,b</sup>

Method of crosslinking	$\text{H}_2\text{SO}_4$	$\text{HCl}$	$\text{NH}_4\text{F}$	Glutaraldehyde + $\text{H}_2\text{SO}_4$ (CN-A-1363414)	Glutaraldehyde + $\text{NH}_4\text{F}$
$\text{CO}_2$ permeance <sup>c</sup>	0.00567	0.00755	0.00837	0.00321	0.0372
$\alpha$ ( $\text{CO}_2/\text{CH}_4$ )	19.0	13.5	1143	21.6	12.0

<sup>a</sup>Membrane preparation: cast PVAm solution on DSS PSO, dried at room temperature, crosslinked with different methods, stored in chamber saturated with water vapour.

<sup>b</sup>All the data measured at 2 bars and room temperature.

<sup>c</sup>Permeance,  $\text{P}/l$ , in units of  $\text{m}^3$  (STP)/ $\text{m}^2\text{bar hr}$ .

The membrane crosslinked by ammonium fluoride showed the best results and the ideal selectivity of  $\text{CO}_2/\text{CH}_4$  was over 1000. This was a much unexpected result.

In order to obtain the carrier effect for  $\text{CO}_2$ , the membrane of the present invention must be kept wet (swollen with water vapour). The proposed carrier mechanism in the wetted membrane is shown in Fig. 3 [8]. It was observed a decrease in permeance when membrane was allowed to dry out, while the original conditions were restored when the membrane again was wetted (Fig. 4).

The present invention comprises membranes having a support structure wherein the MWCO is from about 20,000 to about 40,000, and preferably from about 20,000 to about 30,000. The most preferably support structure is PSO.

- 5 The membranes further comprise PVAm of high molecular weight. In a preferred embodiment the molecular weight is higher than 70,000.

The preferred crosslinking agent of the membranes according to the present invention is  $\text{NH}_4\text{F}$ . To serve as a crosslinking agent also other compounds containing fluoride are  
10 encompassed within the scope of the present invention. Examples of other fluoride containing compounds are ammonium bifluoride ( $\text{NH}_4\text{HF}_2$ ) and hydrofluoric acid (HF).

In general the thickness of selective PVAm layer on the membrane should be as thin as possible in order to increase flux..Preferably the thickness should be  $< 15 \mu\text{m}$ , more  
15 preferred  $< 10 \mu\text{m}$ , even more preferred  $< 5 \mu\text{m}$ , and most preferred  $< 2 \mu\text{m}$ .

In order to keep the membrane wet, the construction of the membrane module is crucial. The membranes according to the present invention should be prepared as a flat sheet type membrane or composite hollow fibres.

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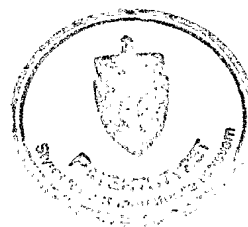
When using the membranes of the present invention for separation of  $\text{CO}_2$ , the process temperature should be kept below the boiling point,  $T_b$ , for water at operating pressure.

To avoid compaction of the swollen membranes of the present invention, the pressure  
25 drop across the membrane,  $\Delta P$ , should be below 80 bar.

### References

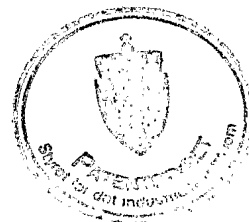
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C l a i m s

1. A composite membrane comprising a support coated with crosslinked polyvinylamine, wherein the crosslinking agent is a fluoride containing compound, and wherein the said membrane is swelled in water vapour.
2. A membrane according to claim 1, wherein the support is flat sheet type or hollow fibres.
3. A membrane according to claim 1, wherein the support has a molecular weight cut-off in the range of from about 20,000 to about 40,000.
4. A membrane according to claim 3, wherein the support is polysulfone.
5. A membrane according to claim 1, wherein the molecular weight of the said polyvinylamine is more than 70,000.
6. A membrane according to claim 1, wherein the crosslinking agent is ammonium fluoride, ammonium bifluoride, or hydrofluoric acid.
7. A membrane according to claim 6, wherein the crosslinking agent is ammonium fluoride.
8. A process for producing a membrane according to claim 1, comprising
  - preparing polyvinlyamine with high molecular weight comprising high degree of amination;
  - coating said polyvinylamine on a support (flat sheet or hollow fibers) to obtain a composite membrane;
  - crosslinking the cast membrane with a fluoride containing compound; and
  - swelling the crosslinked cast membrane in water vapour.
9. Use of a membrane according to claim 1, for separation of CO<sub>2</sub> from gas mixtures.



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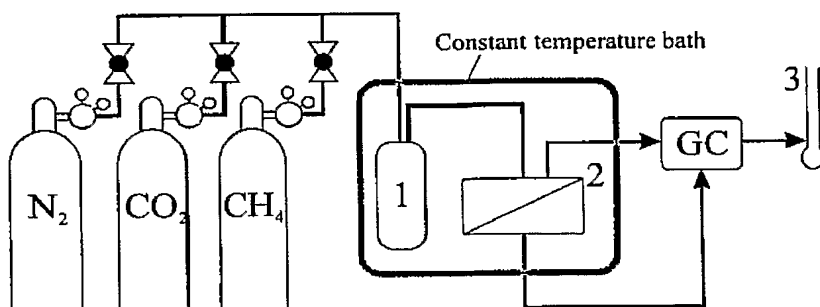
Abstract

O. nr. E34419

The present invention relates to novel fixed-site-membranes comprising a support structure coated with crosslinked polyvinylamine, wherein the crosslinking agent is a fluoride containing compound, and wherein the said membrane is swelled in water vapour. The invention further relates to a process for producing the said membranes, and the use of such membranes for separation of carbon dioxide (CO<sub>2</sub>) from gas mixtures.







1: Humidifier, 2: Flat type membrane cell, 3: flow meter

Fig. 1

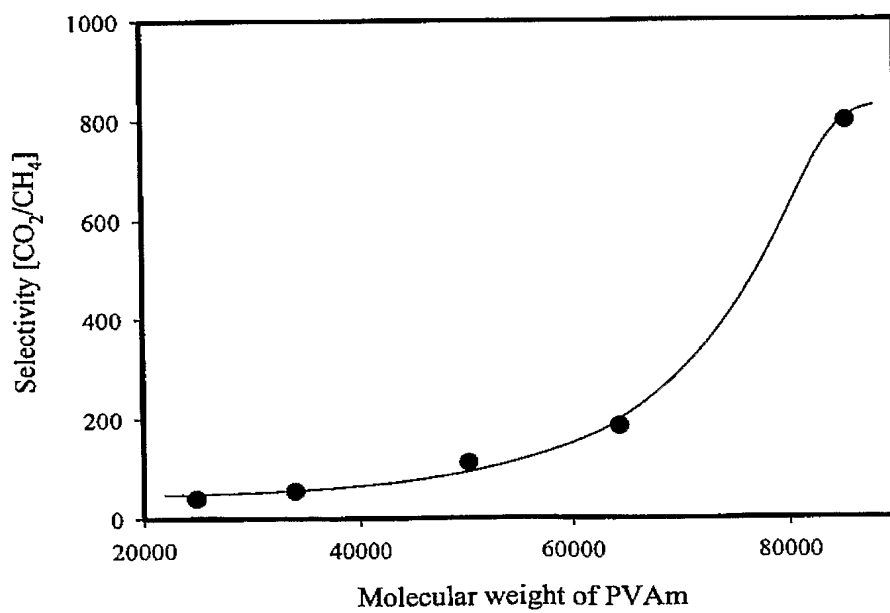


Fig. 2



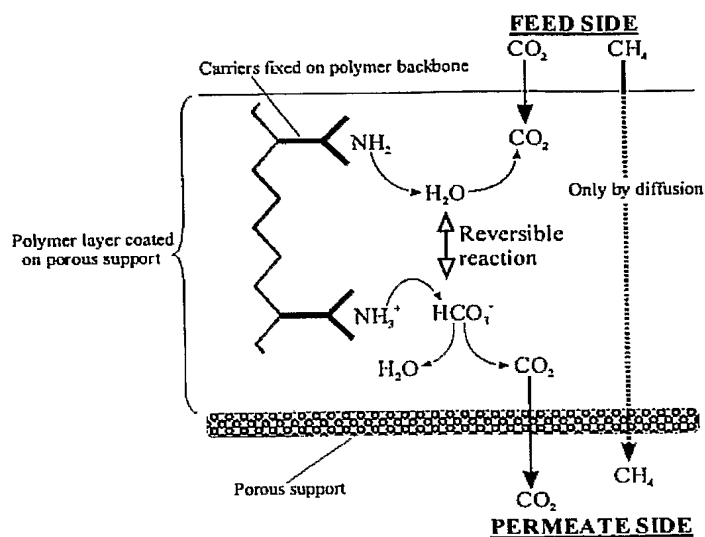
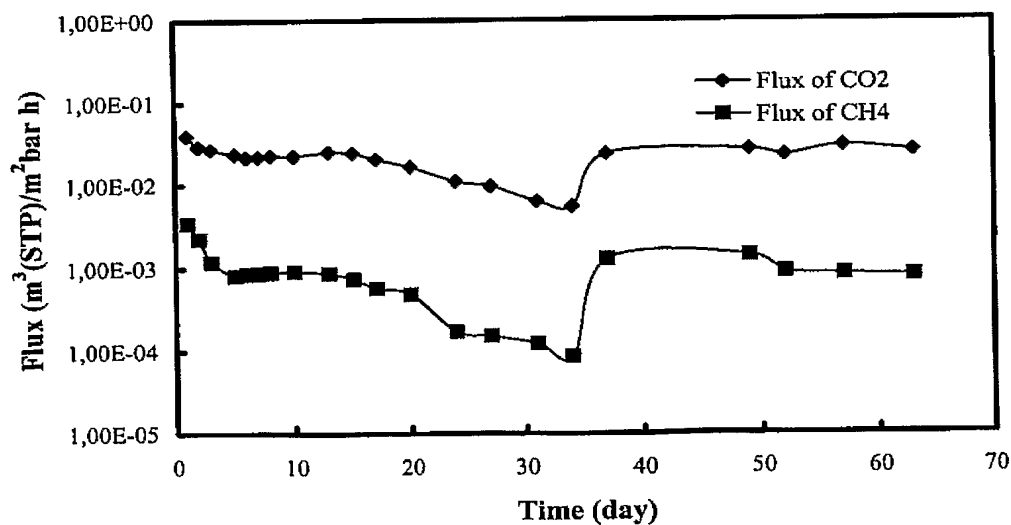
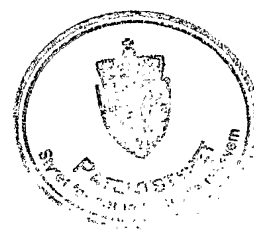


Fig. 3



Perm.flux. of  $\text{CO}_2$  and  $\text{CH}_4$  through the PVAm membrane casted on CA support - after 35 days the membrane is again wetted, and flux is restored.

Fig. 4



# Novel Fixed-Site-Carrier Polyvinylamine Membrane for Carbon Dioxide Capture

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**ABSTRACT:** Fixed-site-carrier membranes were prepared for the facilitated transport of CO<sub>2</sub> by casting polyvinylamine (PVAm) on various supports, such as poly(ether sulfone) (PES), polyacrylonitrile (PAN), cellulose acetate (CA), and polysulfone (PSO). The cast PVAm on the support was crosslinked by various methods with glutaraldehyde, hydrochloric acid, sulfuric acid, and ammonium fluoride. Among the membranes tested, the PVAm cast on polysulfone and crosslinked by ammonium fluoride showed the highest selectivity of CO<sub>2</sub> over CH<sub>4</sub> (>1000). The permeance of CO<sub>2</sub> was then measured to be 0.014 m<sup>3</sup> (STP)/(m<sup>2</sup> bar h) for a 20 μm thick membrane. The effect of the molecular weight of PVAm and feed pressure on the permeance was also investigated. The selectivity increased remarkably with increasing molecular weight and decreased slightly with increased pressure in the range of 1 to 4 bar. © 2004 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 42: 4326–4336, 2004

**Keywords:** composites; membrane; gas permeation; facilitated transport; separation of carbon dioxide

## INTRODUCTION

During the last couple of decades, concern for our global environment has brought into focus the need for CO<sub>2</sub> from anthropogenic sources being captured and brought into storage. In the future, industry will have to comply with strict regulations on CO<sub>2</sub> emissions, hence separation and recovery of CO<sub>2</sub> from gas streams has become of vital importance for industry. CO<sub>2</sub> is usually separated from gas mixtures of H<sub>2</sub>, CO, N<sub>2</sub>, and CH<sub>4</sub> by reversible absorption methods employing var-

ious chemical and/or physical solvents. As the conventional process of treating CO<sub>2</sub> is highly energy consuming, the cost, as well as strict regulations for environmental protection, suggests a need for the development of new energy-efficient processes and more advanced gas-treating technology. The use of a membrane for separation can be one of the more realistic and lower energy consuming methods.<sup>1,2</sup>

Traditionally, thin nonporous polymeric films and microporous materials have been used as membranes. Highly selective membranes with economically feasible permeability have, however, not been reported for conventional polymeric membranes.<sup>1–3</sup>

As an alternative to conventional polymeric membranes, facilitated transport membranes

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have attracted attention because of the potential of achieving both high permeabilities and high selectivities. Facilitated transport membranes may selectively permeate CO<sub>2</sub> by means of a reversible reaction of CO<sub>2</sub> with an incorporated complexing agent (carrier) in the membrane, whereas gases such as H<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> will permeate exclusively by the solution-diffusion mechanism.

The use of facilitated transport membranes for gas separation was first introduced by Ward and Robb<sup>4</sup> by impregnating the pores of a microporous support with a carrier solution. A separation factor of 1500 was reported for CO<sub>2</sub>/O<sub>2</sub>.<sup>4,5</sup> These membranes or supported liquid membranes (SLM) are, however, known to have serious degradation problems like loss of carrier solution because of evaporation or entrainment with the gas stream, and the complexing agent (carrier) can be deactivated. These problems have restricted further development of SLMs. The use of ion exchange membranes as supports was proposed as an approach to overcome the problems of SLMs. The application of ion exchange membranes for the facilitated transport of CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> was first reported by LeBlanc et al.<sup>6</sup> Since then a number of articles have been published on this type of membrane.<sup>7-20</sup> It is suggested by many authors that CO<sub>2</sub> will be transported as carbonate or bicarbonate anions in anion exchange membranes and as anions of various amines in cation exchange membranes. Along with the use of ion exchange membranes as supports, yet another approach to overcome the above limitations was developed by introducing carriers directly into polymer membranes.<sup>21-31</sup> These fixed-site-carrier (FSC) membranes have carriers covalently bonded to the polymer backbone, hence, the carriers have restricted mobility, but are favorable when stability is considered. It is obvious that the diffusivity (and thus permeability) in an FSC membrane is lower than that of a mobile carrier membrane. The diffusivity of a swollen FSC membrane should, however, show diffusivities between that of a mobile and a fixed carrier.

The aminated polymeric membranes for facilitated transport of CO<sub>2</sub> have been investigated extensively in recent years.<sup>15,18-21,27-31</sup> The findings of several of these investigators were that the aminated polymeric membranes showed higher permselectivity in a water swollen condition than in a dry condition. This was also found to be true in the current work.

In the dry membranes, the facilitated transport of CO<sub>2</sub> was expected to be based on the weak acid-base interaction between CO<sub>2</sub> and amine moiety.<sup>27-30</sup> On the other hand, it was assumed that tertiary amino groups such as triethanolamine and 2-(*N,N*-dimethyl)aminoethyl methacrylate acted only as weak base catalysts for the CO<sub>2</sub> hydration reaction in water swollen membranes.<sup>29,30</sup> Therefore, CO<sub>2</sub> does not interact directly with the amino groups fixed to the membrane, but CO<sub>2</sub> is carrier-transported in the form of HCO<sub>3</sub><sup>-</sup>, which gives mobility comparable to that of the mobile carrier membranes (Fig. 1). This theory is also adapted for the membrane reported here. This mechanism may give a possibility of enhanced permeability and selectivity in favor of CO<sub>2</sub> for the aminated fixed-site-carrier membranes comparable to those of the mobile carrier membranes.

This article presents how a specific FSC membrane based on polyvinylamine (PVAm) was synthesized with optimum separation properties for CO<sub>2</sub>, taking into consideration the importance of parameters like molecular weight, crosslinking agent, and membrane support structure. The obtained experimental data for permeance and selectivity are discussed. The theory of facilitated gas transport through the membrane is briefly presented.

## BACKGROUND: FACILITATED TRANSPORT

As described in the previous paragraph, it is assumed that CO<sub>2</sub> is selectively carrier-transported as a bicarbonate anion through the swollen FSC membrane. The method used for crosslinking may also contribute in a positive way to the selective transport of CO<sub>2</sub>. Quinn et al.<sup>32-34</sup> suggested the possible role of fluoride ions in facilitated transport in a swollen membrane, as illustrated in Figure 2. The water molecule becomes more basic than pure bulk water when it is hydrogen bonded to a fluoride ion, and the fluoride is creating highly polar sites in the membrane. The basic water molecule has an increased affinity for CO<sub>2</sub> that leads to increased concentration of HCO<sub>3</sub><sup>-</sup> in the membrane and a consecutively increased transport of CO<sub>2</sub>. The permeation of gases like CH<sub>4</sub>, N<sub>2</sub>, and O<sub>2</sub> will be blocked by the highly polar sites in the membrane because of low solubility of these nonpolar gases, and an increased selectivity should be expected. This is also documented in the current work. As elaborated previ-

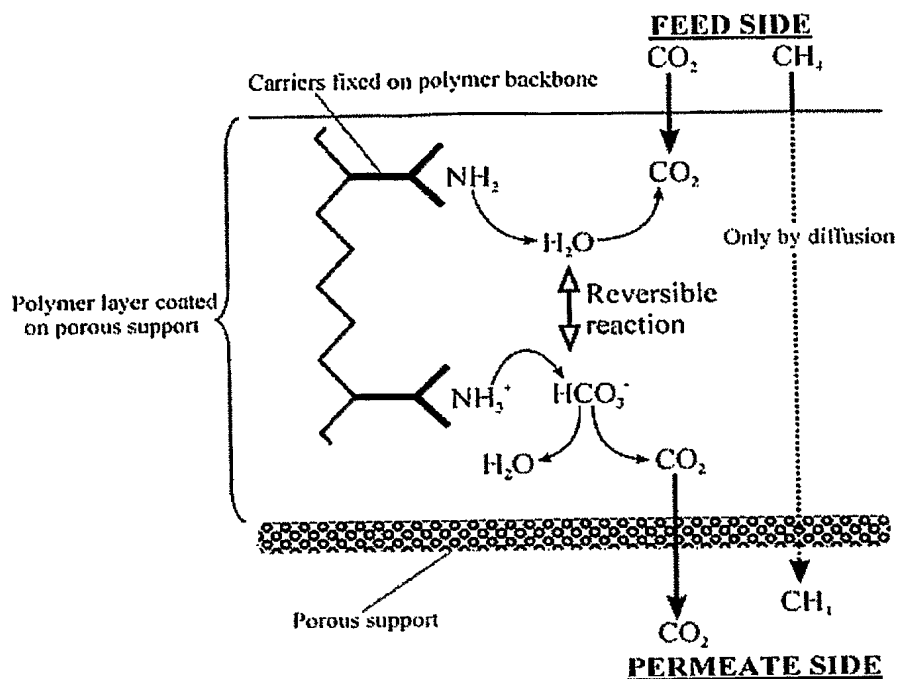


Figure 1. A proposed mechanism of facilitated transport in a fixed-site-carrier membrane.

ously, the characteristic of a facilitated or carrier-mediated transport is the occurrence of a reversible chemical reaction or complexation process in combination with a diffusion process. This implies that either the diffusion or the reaction is rate-limiting: For the membrane in the current study, the diffusion is assumed to be rate-limiting. The total flux of a permeant *A* (here CO<sub>2</sub>) will thus be the sum of both the Fickian diffusion and the carrier-mediated diffusion, as illustrated in eq 1<sup>35</sup>

$$J_A = \frac{D_A}{l} (c_{A,0} - c_{A,l}) + \frac{D_{AC}}{l} (c_{AC,0} - c_{AC,l}) \quad (1)$$

$$c_A = S_A p_A \quad (2)$$

where the first term on the right hand side of eq 1 is the Fickian diffusion ( $D_A$ ), and the second term represents the carrier mediated diffusion ( $D_{AC}$ ). The thickness of the membrane is  $l$ , whereas  $c$  is the concentration of the component *A* and its complex *AC* at the interfaces of the membrane, 0 and  $l$ , on the feed and permeate side, respectively. The concentration difference of the complex *AC* in eq 1

must be further expressed by an equilibrium constant of the complexing reaction and a distribution coefficient. This is given in detail by Cussler.<sup>35</sup> The nonpolar gases in the gas mixture will exclusively be transported through the membrane by Fickian diffusion. With partial pressures ( $p_A$ ) instead of concentration  $c_A$  (inserting eq 2 into eq 1, it can easily be seen that the driving force over the membrane will be the dif-

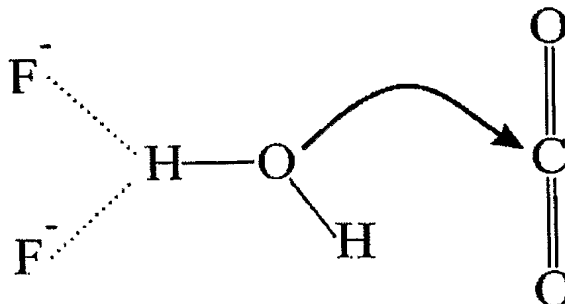


Figure 2. A proposed role of fluoride ion in facilitated transport.

ference in partial pressures for the Fickian diffusion, and that transport also will depend on the solubility coefficient,  $S_A$ , for the gas in the polymer. For the carrier-mediated transport, the driving force will be the concentration difference of the complex AC over the membrane. As mentioned previously, the permeation of the nonpolar gases may additionally be hindered because of the highly polar sites in the membrane caused by the presence of fluoride ions. This should then lead to an increased permeance of CO<sub>2</sub> compared to gases like CH<sub>4</sub>, N<sub>2</sub>, and O<sub>2</sub>, giving high selectivities in favor of CO<sub>2</sub> (as illustrated in Figure 2).

## EXPERIMENTAL

FSC membranes were prepared by coating PVAm on various supports such as poly(ether sulfone) (PES), polyacrylonitrile (PAN), cellulose acetate (CA), and polysulfone (PSO). The cast PVAm on the support was crosslinked by various methods with glutaraldehyde, hydrochloric acid, sulfuric acid, and ammonium fluoride. The effect of the molecular weight of PVAm and feed pressure on the permeance was investigated. The permeance and selectivity of the membranes were measured in a water swollen condition, and also over time (70 days) by allowing the water to partly evaporate.

### Acrylamide Polymerization

Polymerization of acrylamide (CH<sub>2</sub>=CH—CO—NH<sub>2</sub>; Merck) was carried out in a four necked jacketed reactor kept at 45 °C. Ammonium persulfate [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] and sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>) were used as initiators. Persulfate was decomposed by a sulfite ion as the reducing agent. The concentration and the ratio of the initiator solutions were chosen to obtain polyacrylamide (PAA)  $\{—[CH_2—CH(CO—NH_2)]_n—\}$  with a suitable molecular weight to go to the next stage. In a typical procedure, acrylamide (16.5 g; 0.23 mol) was dissolved in distilled water (248 mL) and the solution was mechanically stirred under a nitrogen atmosphere for 1 h to remove oxygen. A concentrated solution of ammonium persulfate [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>; 234.8 mg; 1.03 mmol] in water (10 mL) and of sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>; 130.5 mg; 1.21 mmol) in water (10 mL) were added, respectively. The polymerization was allowed to proceed at 45 °C for 5 h and 55 °C for 2 h. The molecular weight of the resulting PAA was determined by

measuring the viscosity of the diluted polymer solution. The intrinsic viscosity of PAA in the water solution was determined with an Ubbelohde viscometer with suspended level bulb size: = 0.009825 (Schott-Gerate GmbH, Germany). The number-average molecular weight of PAA,  $M_n$ , was calculated from the following Mark-Houwink relation:  $[\eta]/(dL \times g^{-1}) = 6.8 \times 10^{-4} M_n^{0.66}$  where  $dL = 100$  mL and  $[\eta]$  is the intrinsic viscosity in water at 30 °C.<sup>36,37</sup>

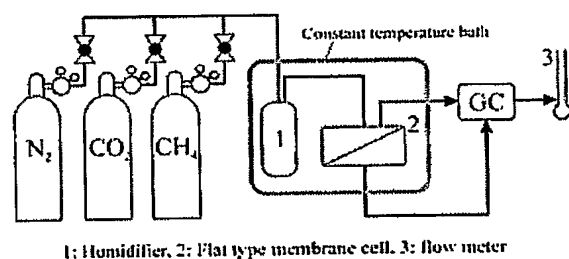
### Preparation of Polyvinylamine by the Hofmann reaction of Polyacrylamide

The Hofmann reaction was suggested as a quick and convenient method of preparing PVAm from PAA by Tanaka et al.,<sup>38–40</sup> whereas Achari et al.<sup>37</sup> proposed that PVAm could be prepared from PAA by the Hofmann reaction with a high degree of amination (more than 90%), keeping the extent of side reactions to a very low level by careful control of reaction parameters.

In a typical reaction,  $\alpha$  (molar ratio of [NaOCl]/[amide]) and  $\beta$  (molar ratio of [NaOH]/[amide]) were 1 and 27, respectively. The following three steps were carried out: (1) A 6.2 wt % solution of PAA in water (12.4 g of PAA in 200 g of solution; 0.17 mol of amide function) was added to a mixture of 11.63 mL of 15 M NaOH (0.17 mol) and 39.73 mL of 4.39 M NaOCl (13% active Cl; 0.17 mol; Acros, NJ); at -10 °C with vigorous stirring. (2) After 1.5 h, 302.34 mL of 15 M NaOH (4.54 mol) was added. (3) The temperature of the reaction mixture was kept at -10 °C for 0.5 h; then increased to 0 °C and kept there for 17 h (with stirring). The resulting polymer was isolated by pouring the reaction mixture into methanol (of about equal volume) and dissolving it in water. The solution was then titrated with 5 M HCl to pH 2, and the polymer was isolated as hydrochloride from methanol. Finally, the polymer was dissolved in water to a concentration of 5–10%; suitable for membrane casting. The  $M_n$  of PVAm was determined by the following relation:  $[\eta]/(dL \times g^{-1}) = 6.2 \times 10^{-3} M_n^{0.88}$  where  $dL = 100$  mL and  $[\eta]$  is the intrinsic viscosity in 0.01 M NaOH/0.1 M NaCl at 25 °C.<sup>37,40</sup> Main reaction:  $R—CO—NH_2 + NaOCl + 2NaOH \rightarrow RNH_2 + Na_2CO_3 + NaCl + H_2O$ .

### Membrane Preparation

Two microporous polysulfone flat sheet support membranes (PSO) were tested; one with a molec-



**Figure 3.** Experimental setup for gas permeation measurement.

ular weight cutoff (MWCO) of 20,000 [from Danish Separation Systems AS (DSS)] and one with a MWCO of 30,000 (from Osmonics Vista Operation). The following supports were also tested: PES (MWCO = 10,000), CA (MWCO = 20,000), and PAN (MWCO = 75,000) (all three from Osmonics Vista Operation).

The support membrane was cut into suitable pieces and taped to a clean, horizontally leveled glass plate. The casting polymer solution of PVAm in water was poured onto the support, and the film thickness was adjusted by a casting knife to approximately 20  $\mu\text{m}$ . The casting was left to evaporate at room temperature for at least 6 h. The dried cast membranes were crosslinked by different procedures to find the optimum method:

1. Glutaraldehyde (50%, 30 min);
2. Glutaraldehyde (50%, 30 min), and then  $\text{H}_2\text{SO}_4$  (pH = 1, 10–30 min);
3.  $\text{NH}_4\text{F}$  (0.5 M, 2 h);
4. Glutaraldehyde (50%, 30 min), and then  $\text{NH}_4\text{F}$  (0.5 M, 2 h);
5.  $\text{H}_2\text{SO}_4$  (pH = 1, 10–30 min) or  $\text{HCl}$  (pH = 1, 10–30 min).

Care was taken to ensure the membrane was leveled during drying and crosslinking processes. Several attempts were necessary to obtain an even membrane free of defects. The crosslinked membranes were stored in a chamber saturated with water vapor at room temperature.

#### Membrane Testing

Permeability of the membranes was measured with an apparatus equipped with a humidifier (Fig. 3). A membrane (diameter 50 mm, thickness  $\sim 20 \mu\text{m}$ ) was placed on a porous metal disk in a flat type membrane cell and sealed with rubber

O-rings. The feed gas was saturated with water vapor by a humidifier. The feed and permeate flow rates were measured by a bubble flow meter. All experiments were conducted in a constant temperature environment within the range of 25–35  $^{\circ}\text{C}$ . The pressure difference between the feed and the permeate sides was 2–4 bar. A more extensive description for determination of both permeabilities and selectivities has been given elsewhere.<sup>41</sup>

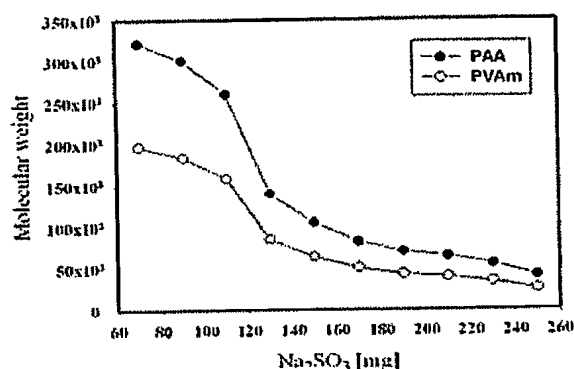
The permeance (flux) was calculated as  $P/l$  in the units  $\text{m}^3(\text{STP})/(\text{m}^2 \text{ bar h})$ . The flux will be strongly dependant on the thickness of the membrane, and the permeation will be inversely proportional to the thickness. For the membrane reported, the thickness will be brought down from 20 to 2  $\mu\text{m}$  in further development, which should result in a flux 10 times those reported here.

## RESULTS AND DISCUSSION

### Polymerization, Hofmann Reaction, and Molecular Weight

The solution of acrylamide (AA) under polymerization conditions could easily be converted to an unwanted gel state, especially when seeking to obtain a higher molecular weight of PAA. For example, increasing the initial concentration of AA and decreasing the initiator concentration led to severe gelation of the reaction solution. PAA with a different molecular weight could be obtained by controlling the concentration of initiators, whereas the concentration of AA, reaction temperature, and time were fixed (Fig. 4). Several trials were carried out to find suitable conditions.

The Hofmann reaction scheme of PAA was presented by Achari et al.,<sup>37</sup> involving three mechanistic stages of *N*-chlorination of the amido group, hydrogen abstraction, rearrangement of the *N*-chlorinated anion, and acidic conversion into an amino group of the sodium carbamate. Each reaction stage was controlled by temperature and the use of initiators at fixed molar ratios:  $\alpha$  (molar ratio of  $[\text{NaOCl}]/[\text{amide}]$ ) and  $\beta$  (molar ratio of  $[\text{NaOH}]/[\text{amide}]$ ); 1 and 27, respectively. Much care had to be taken to prevent the reaction mixture from gelating or freezing at the low temperature of  $-10 \text{ }^{\circ}\text{C}$ . The side-reactions could be kept to a low level, and analysis showed that the amino group content in PVAm was over 90% in mol. The obtained product was a hygroscopic white solid.



**Figure 4.** Molecular weight of PAA and PVAm as a function of the amount of Na<sub>2</sub>SO<sub>3</sub> [molar ratio of Na<sub>2</sub>SO<sub>3</sub>/(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> = 1.17; AA 16.5 g in 248 mL of water].

## The Composite Membranes

### Crosslinking

Different crosslinking procedures for PVAm were tested out, and permeance was measured for the composite membrane (see Membrane Preparation). The membranes crosslinked by glutaraldehyde were swelling. The crosslinking took place only on the surface; hence became a barrier for further diffusion of glutaraldehyde into the internal layer of PVAm and inhibited any further crosslinking reaction. The internal PVAm was therefore swelling severely when combined with water, and a good membrane could not be obtained. If the swelled membrane was immersed in dilute acid solution for awhile, it obtained a dense, smooth, nice looking surface. The hydrogen bonding was assumed to be the main reason. The membranes crosslinked by acids (H<sup>+</sup>) or fluoride (F<sup>-</sup>) showed a smooth and even but somewhat sticky, gelatinized surface. The results of

permeance measurements for different crosslinking methods are reported in Table 1 for membranes cast on a PSO support. As can be seen, the best results with respect to selectivity are obtained with NH<sub>4</sub>F as a crosslinking agent. The absence of a crosslinked PVAm layer or a layer with defects would result in low selectivity.

### Support Materials

Five different support materials were tested (see Membrane Preparation). As documented in Table 2, the PSO (from Danish Separation Systems AS, DSS) showed the highest selectivity for CO<sub>2</sub>/CH<sub>4</sub>, whereas CA and PAN have high permeance, but very low selectivity. It was therefore decided to focus on the PSO support material for further development of the composite membrane, and to try to increase the CO<sub>2</sub> permeance.

As shown in Figure 5(1), a layer of PVAm [molecular weight (MW) ~34,000] was clearly formed on the PSO with MWCO = 20,000 (DSS). The thickness of the layer was about 5–10 μm, which was less than the expected thickness of 15–25 μm estimated by simple calculation of the concentration and the amount of the casting solution poured onto the support. This may imply that the structure of the skin layer contracted during crosslinking process or part of the casting solution leaked into the support. In some cases, the PVAm of lower molecular weight (MW ~25,000) did not make an apparent layer on the same DSS PSO [Fig. 5(3)]. For PVAm (MW ~39,000) coated on PSO from Osmonics (MWCO = 30,000), the layer is hardly visible [Fig. 5(2)], and it is clear from the SEM image that the PVAm solution here has leaked into the PSO support instead of forming a layer on top. From these observations, combined with results from permeance measurements, it was concluded that there ought to be a

**Table 1.** Comparison of Permselectivity for PVAm Membranes Cast on PSO Support using Different Crosslinking Methods<sup>a,b</sup>

Method of crosslinking	H <sub>2</sub> SO <sub>4</sub>	HCl	NH <sub>4</sub> F	Glutaraldehyde + H <sub>2</sub> SO <sub>4</sub>	Glutaraldehyde + NH <sub>4</sub> F
CO <sub>2</sub> permeance <sup>c</sup>	0.00567	0.00755	0.00837	0.00321	0.0372
α (CO <sub>2</sub> /CH <sub>4</sub> )	19.0	13.5	1143	21.6	12.0

<sup>a</sup> Membrane preparation: cast PVAm solution on DSS PSO, dried at room temperature, crosslinked with different methods, and stored in a chamber saturated with water vapor.

<sup>b</sup> All the data measured at 2 bar and room temperature.

<sup>c</sup> Permeance, P/l, in units of m<sup>3</sup> (STP)/m<sup>2</sup> bar h.



**Table 2.** Comparison of Permselectivity for PVAm Membranes on Different Support Materials<sup>a,b</sup>

Support	PSO (DSS)	PSO (Osmonics)	CA	PAN	PES
CO <sub>2</sub> permeance <sup>c</sup>	0.00837	0.0063	0.099	0.0327	0.00388
$\alpha$ (CO <sub>2</sub> /CH <sub>4</sub> )	1143	26.9	17.3	5.1	6.5

<sup>a</sup> Membrane preparation: cast PVAm solution on supports, dried at room temperature, crosslinked with NH<sub>4</sub>F, and stored in a chamber saturated with water vapor.

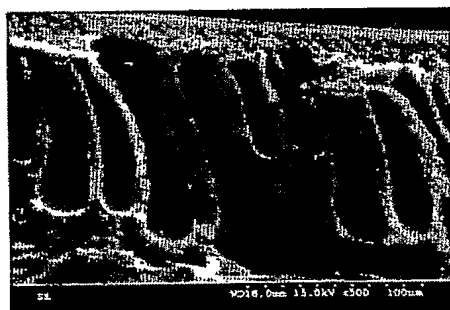
<sup>b</sup> All the data measured at 2 bar and room temperature.

<sup>c</sup> Permeance, P/l, in units of m<sup>3</sup> (STP)/m<sup>2</sup> bar h.

reasonable difference (>20,000) between the average molecular weight of PVAm and the MWCO of the support material to obtain a selective PVAm layer on the top. This may also explain the low selectivity obtained with the Osmonics PSO compared to the DSS PSO—however, this was not investigated further because detailed information on the support materials was difficult to obtain from the supplier.

#### Discussion of Permselectivity Results

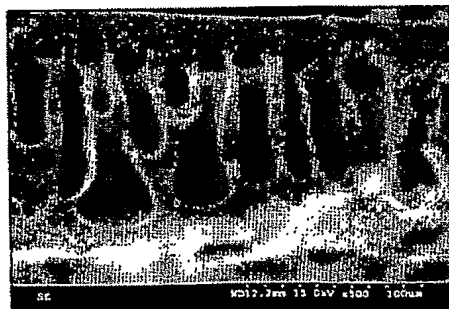
Based on the initial results from different crosslinking procedures and composite membrane preparation reported above, it was expected that a composite membrane prepared with PVAm of relatively high-molecular-weight, crosslinked with a fluoride compound and cast on DSS PSO, would show high selectivity for CO<sub>2</sub>/CH<sub>4</sub>.



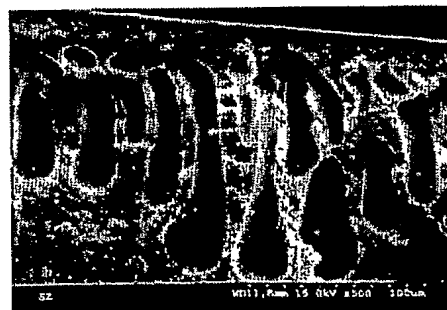
1 - PVAm (MW 34,000) on DSS PSO



2 - PVAm (MW 39,000) on Osmonics PSO

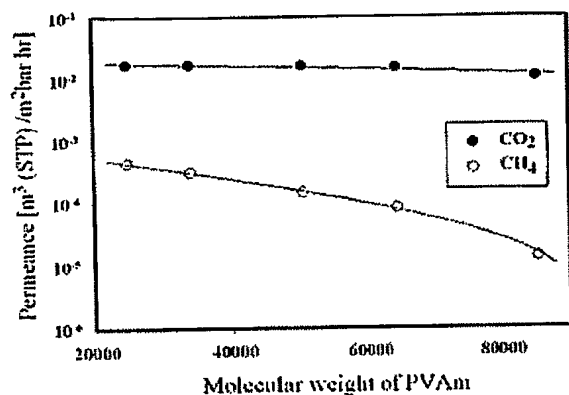


3 - PVAm (MW 25,000) on DSS PSO



4 - DSS PSO

**Figure 5.** SEM cross-sections of different PVAm/PSO membranes after being crosslinked with NH<sub>4</sub>F treatment. All DSS PSO with MWCO = 20,000; Osmonics PSO with MWCO = 30,000.



**Figure 6.** Effect of molecular weight of PVAm on permeance of CO<sub>2</sub> and CH<sub>4</sub> at 35 °C, 3 bar. Membrane preparation: cast PVAm solution on DSS PSO, dried at room temperature, crosslinked with NH<sub>4</sub>F.

The results of different crosslinking methods are shown in Table 1. As can be seen, of the five crosslinking methods tested, crosslinking with NH<sub>4</sub>F shows the best selectivity. This is in agreement with Quinn et al.,<sup>32–34</sup> who suggested the possible role of the fluoride ion in facilitated transport, as illustrated in Figure 2 and explained in the section Background for Facilitated Transport. The number of available *carrier sites* for transport of CO<sub>2</sub> in the membrane (see Fig. 1) will be a function of the degree of amination achieved by the Hofmann reaction and the amount of crosslinking agent used. At the same time, the permeance of the gases will be a function of the molecular weight. As shown in Figure 6, the CO<sub>2</sub> permeance decreased slightly with the increasing molecular weight of PVAm, whereas CH<sub>4</sub> permeance showed a major decrease. The decrease of permeance for both gases is not surprising because the mobility of polymer chain segments and permeating species are more restricted in higher molecular weight polymers with long chains. Additionally, the permeance of the nonpolar CH<sub>4</sub>, of which the transport only depends on a solution–diffusion mechanism, was affected both by the restricted mobility of the chains and by the highly polar fluoride ions introduced as the crosslinking agent. For the CO<sub>2</sub> permeance, where the facilitated mechanism is believed to be the dominating method of transport, the permeance showed only a minor decrease. The increase in selectivity for CO<sub>2</sub>/CH<sub>4</sub> is dramatic when plotted as a function of molecular weight

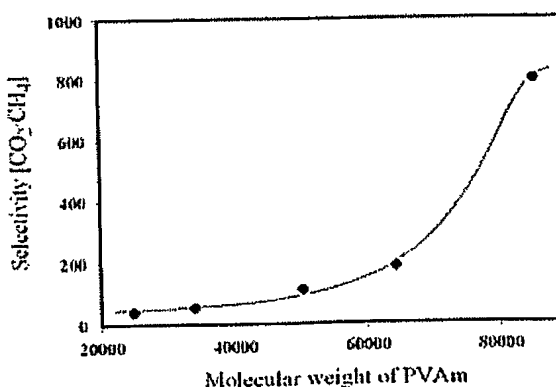
(see Fig. 7). Further investigation of the effect of molecular weight will be carried out for a more extensive range, as well as permeation tests for N<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub> to compare with CO<sub>2</sub>. The results obtained in the current work are compared with others reported for FSC membranes<sup>28,30,31,42</sup> in Table 3. The data presented in Figures 6 and 7 are mean values from a series of 5–7 experiments. The standard deviation is approximately 7%.

#### Feed Pressure

A few data on the effect of feed gas pressure on the permeance of CO<sub>2</sub> and CH<sub>4</sub> in a PVAm/PSO membrane were obtained (Fig. 8). In the range of 2–4 bar, the permeance of CO<sub>2</sub> was almost maintained. This could indicate that the carrier sites for CO<sub>2</sub> became saturated as pressure increased, and that transport because of the solution–diffusion mechanism became more important. The net result would be no change. The permeance of CH<sub>4</sub> increased slightly, most likely because of enhanced sorption according to the solution–diffusion mechanism. A slight decrease in selectivity resulted. Further work is needed to check the effect of pressure on the CO<sub>2</sub>-selective FSC-membrane.

#### Durability

In the early phase of the project, a swollen PVAm membrane cast on CA was tested for more than 2 months, and the selectivity of CO<sub>2</sub>/CH<sub>4</sub> was maintained (Fig. 9). An increase in selectivity and a decrease in permeance was observed if the wa-



**Figure 7.** Effect of molecular weight of PVAm on ideal selectivity of CO<sub>2</sub>/CH<sub>4</sub> at 35 °C, 3 bar. Membrane preparation: cast PVAm solution on DSS PSO, dried at room temperature, crosslinked with NH<sub>4</sub>F.

**Table 3.** Comparison of Membrane Separation Properties Obtained in Current Work with Values Reported for Other Fixed-Site-Carrier Membranes<sup>42</sup>

Membrane	Selectivity	Flux <sup>a</sup>	System	$\Delta P_{\text{CO}_2}^b$ (bar)	Ref.
Polymerized membrane from diisopropylamine	17	1.2	CO <sub>2</sub> /CH <sub>4</sub> 3.5 vol % CO <sub>2</sub>	—	28
Poly (2-(N,N-dimethyl) aminoethylmethacrylate)	130	$2.7 \times 10^{-3}$ $-2.7 \times 10^{-2}$	CO <sub>2</sub> /N <sub>2</sub> 2.7–58 vol % CO <sub>2</sub>	0.05	30
Polyethylenimine/poly(vinyl-alcohol)	230	$2.7 \times 10^{-3}$	CO <sub>2</sub> /N <sub>2</sub> 5.8–34.4 vol % CO <sub>2</sub>	0.07	31
Membrane from polyvinylpyrrolidone by hydrolysis	48.1 39.3	$4.6 \times 10^{-1}$ $1.2 \times 10^{-1}$	CO <sub>2</sub> /CH <sub>4</sub> 50 vol % CO <sub>2</sub>	0.02 0.07	42
Membrane from polyvinylpyrrolidone by hydrolysis	212.1 155.9	2.1 $4.4 \times 10^{-1}$	Pure CO <sub>2</sub> and CH <sub>4</sub>	0.01 0.07	42
Polyvinylamine on polysulfone support	700–1100	$8.4 \times 10^{-3}$ $-1.0 \times 10^{-2}$	Pure CO <sub>2</sub> and CH <sub>4</sub>	2–4	this work

<sup>a</sup> The units of flux and pressure are converted to units used in the current paper (m<sup>3</sup> (STP)/m<sup>2</sup> bar hr).

<sup>b</sup>  $\Delta P$  represents the approximate partial pressure difference over the membrane (feed-permeate side).

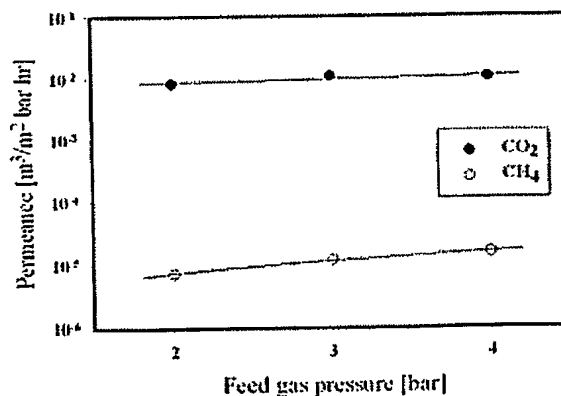
ter was allowed to evaporate from the membrane during this period. As can be seen from Figure 9, the permeance and selectivity was restored when water was again fed to the membrane. The same effect is expected for the swollen and highly selective PVAm on PSO; however, this is still to be documented. It was concluded that the permselectivity of the membrane depended on the membrane being kept swollen, and that water worked as a mobile medium for the transport of CO<sub>2</sub> and thus kept the amino groups active. The gas feed to the membrane should at all times be saturated with water vapor to prevent the membrane from drying out. Quinn et al.<sup>33</sup> suggested that if selectivity decrease was observed with increasing humidity in facilitated transport membranes, it could be because of dilation of the active layer structure caused by an increase in water content.

## CONCLUSIONS

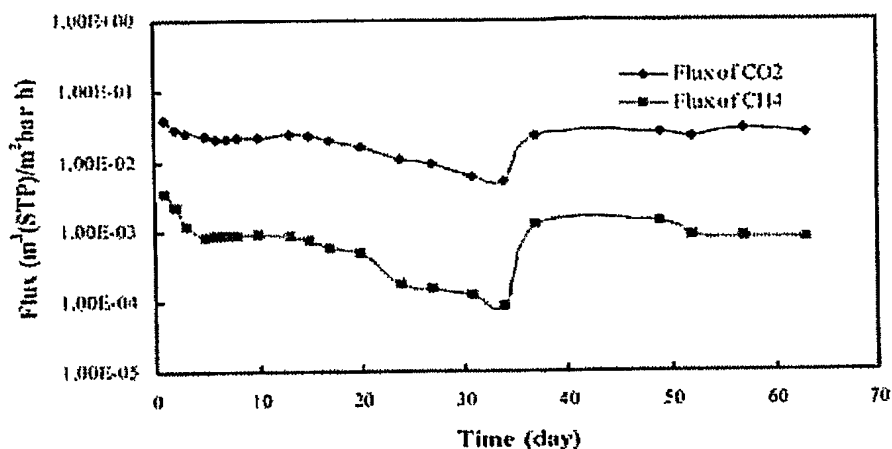
1. The choice of proper support material proved to be very important to maximize the facilitated transport in the novel synthesized FSC-membrane. Polysulfone supported membranes showed the best permselectivity of carbon dioxide over methane.
2. The membranes were crosslinked by different agents, and among these, ammonium fluoride showed the best result, giving an ideal selectivity of CO<sub>2</sub>/CH<sub>4</sub>, over 1000. The advantage

of the crosslinking with NH<sub>4</sub>F is both to make a denser coating layer and to keep amino groups active for CO<sub>2</sub> facilitated transport.

3. For the same crosslinkage condition, the increase in molecular weight for polyvinylamine resulted in a slight decrease in permeation for CO<sub>2</sub> and a major decrease for CH<sub>4</sub>, hence giving a remarkable increase in selectivity. This was explained by the restricted mobility in higher molecular weight membranes. Further investigations are necessary.



**Figure 8.** Effect of feed gas pressure on permeance of CO<sub>2</sub> and CH<sub>4</sub> in PVAm/PSO membrane at 35 °C. Molecular weight of PVAm: 85,400. Membrane preparation: cast PVAm solution on DSS PSO, dried at room temperature, crosslinked with NH<sub>4</sub>F.



**Figure 9.** Permeation flux of CO<sub>2</sub> and CH<sub>4</sub> as a function of time in a swollen PVAm membrane on CA support (crosslinked with NH<sub>4</sub>F). Water was allowed to evaporate during the first 35 days of the experiments, then water was added and flux and selectivity were restored.

4. The permeance of CO<sub>2</sub> was maintained, whereas the permeance of CH<sub>4</sub> increased slightly with increasing pressure in the range of 1–4 bar. This pressure dependence was explained by the competition between the facilitated transport mechanism and the solution–diffusion mechanism. Further work will be carried out to clarify this.
5. The PVAm/PSO membrane was tested continuously for approximately 2 months and proved to be stable over this length of time. When water was allowed to evaporate from the membrane, a selectivity increase was observed, whereas permeance increased when the membrane again was wetted. It was concluded that water in the membrane is acting as a mobile medium for transport of CO<sub>2</sub> and keeping amino groups active.

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